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The Effect of Impurities on the Electrodeposition of Zinc from Zinc Sulfate Solution Containing Antimony.

Emmitt L. Klebba

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A Thesis
Submitted to the Department of Chemistry
in Partial Fulfillment of the
Requirements for the Degree of
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THE EFFECT OF IMPURITIES ON THE ELECTRODEPOSITION OF ZINC FROM ZINC SULFATE SOLUTION CONTAINING ANTIMONY.

It has been proven by research and years of experience, that before electrolytic zinc is possible, the electrolyte, as zinc sulfate solution must be prepared as pure as is economical. In other words, the ideal electrolyte must only be a solution of one metal - zinc. Every other metal and carbon must be excluded if good recovery and a firm deposit is to be obtained.

The electrolyte used in the commercial production of electrolytic zinc is termed "Pure Solution", however, in reality it is impure. The alkaline earth and alkali metals along with the more chemically active metals are not precipitated by the procedure used in commercial practice. They are, therefore, allowed to build up in quantity. These common impurities seem to have no effect on deposition, yet their role in the solution cannot be ignored.

One thing in common to both laboratory and practice of industry is that certain impurities in the electrolyte have definite injurious effects on the cathode deposit. Antimony is one of these notorious offenders. When it is present in the solution, the cathode deposit is seriously affected. These effects may be as "trees", poor current efficiency, or if a neutral solution is used, a sponge deposit. When this

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sponge deposit is produced, it has absolutely no refining value due to the fact that it readily oxidizes on being gently heated. With the results of this so called "evil" readily reproducible, it was decided at this time to determine the "effects" of other impurities on these so called "features". It was decided to ascertain whether the properties were diminished or exaggerated by the mixing of the other impurity with the antimony present in the solution.

REAGENTS

The electrolyte used in this problem was as chemically pure as was possible to obtain under the present conditions. Anaconda electrolytic zinc dust well over 99.99 per cent pure was dissolved in chemically pure sulfuric acid. Recrystallized copper sulfate was added to the above pulp. The addition of copper sulfate to the zinc is for the purpose of hastening the reaction between zinc and sulfuric acid. The chemically pure zinc is very slow to react with sulfuric acid, but on the addition of copper sulfate, metallic copper is precipitated and the hydrogen overvoltage is reduced. The hydrogen overvoltage on copper is less than one half that on zinc so the reaction goes on with great rapidity. There is no fear of copper going into solution as long as excess zinc is present. For this reason, twice the theoretical amount of zinc required was used.

The solution is further purified by the action of the copper - zinc couple which precipitates all metals noble to zinc that may be present in the "dust".

The volume of sulfuric acid used for the preparation of each stock solution was two and one half liters. The zinc consumption was 6500 grams. Copper sulfate added amounted to one hundred grams. The volume of distilled water added was sixteen liters.

The solution during its preparation was frequently agitated to allow the gases to escape and permit the zinc to settle. As soon as action ceased the liquid was decanted, filtered, diluted to the desired zinc concentration (one hundred grams of zinc per liter), and bottled. The remaining solids, zinc and copper, were rejected. This stock solution before dilution approximates one hundred eighty grams of zinc per liter of solution. The free acid present after the reaction is about nil.

Antimony was put in solution by adding a small quantity of antimony trioxide to two liters of boiling zinc sulfate solution. The whole is agitated for a time and then allowed to cool. The antimony content of the solution was determined by Lowe's method, i. e., the permanganate titration procedure.

APPARATUS

The electrolyses were conducted in a tall beaker of five hundred cubic centimeters capacity. This type was decided upon after other forms had been found unsatisfactory.

The cathodes used in this problem were exclusively of the highest grade "Anaconda" electrolytic zinc.

The small slabs obtained were first broken into four sections. These pieces were then heated in an oil bath at 150° Centigrade and then rolled to the desired thickness (0.01"). At this temperature, the zinc rolls easily and does not crack. The control of the bath temperature leads to the success in zinc rolling.

The cathode immersion area was 9.3 square centimeters. This value was used for the sake of convenience; the milliammeter reading for this area of immersion was the current density per square foot.

The cathode strips were two centimeters wide, ten to twelve centimeters long, and weighed approximately three grams.

The top of the cathode strip was punched so that the electrode could be suspended while weighing, thereby reducing the danger of stripping the "trees" and obtaining incorrect results for current efficiency.

Prior to deposition, each cathode was dipped in dilute nitric acid to remove all soluble salts, then rinsed in distilled water, rewashed with ethyl alcohol, ignited, and weighed.

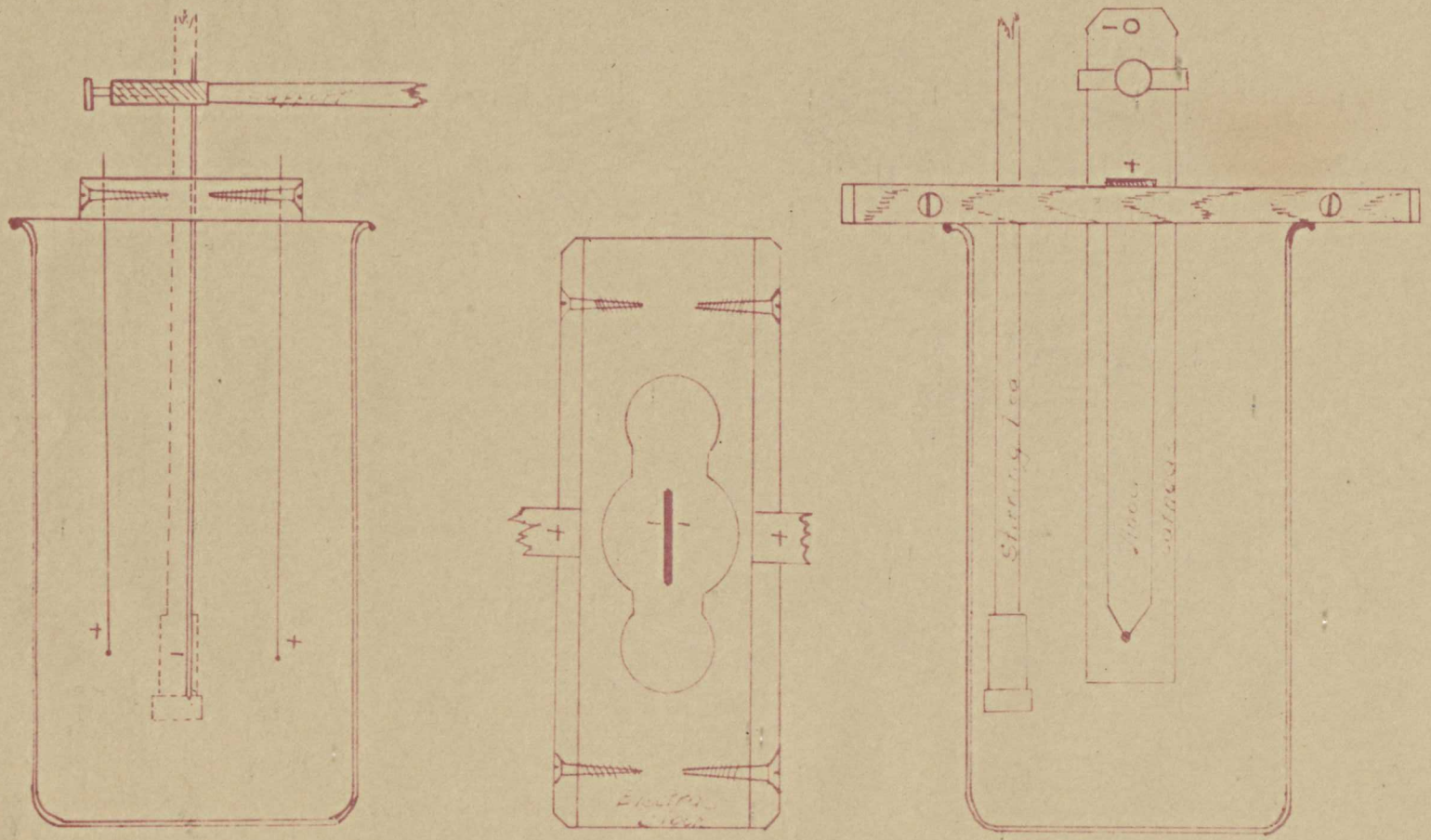
The anodes used in these determinations were of chemically pure sheet lead. There was one of these anodes on either side of the cathode. Their immersion area was approximately one square centimeter.

Circulation was maintained by the use of an electric mechanical stirrer. Gas evolution was not considered as an effective agitator, however, it does help.

There was no provision made for temperature control. The current during electrolysis was not sufficient or result in noticeable "heating". The temperature of the operation may, therefore, be considered as that of the laboratory, near 20° Centigrade.

The method of cathode suspension proved by far to be best for the problem. It can best be studied from the illustration, Figure 1.

When electrolysis was about to commence, the current was turned on and the circuit was closed by immersing the cathode in the electrolyte. After about twenty minutes, the circuit is broken by raising the cathode. The cathode strip is carefully washed to remove adherent solution. The water is washed off with ethyl alcohol and the whole is ignited.



Detail of Electrodes & Cell.

Figure 1.

A copper coulometer cell was connected in series with the zinc cell, which made it possible to determine the quantity of current that has passed during the operation.

The volume of electrolyte used in the majority of determinations was two hundred cubic centimeters.

PROCEDURE

The first part of the problem was mainly to determine the maximum amount of antimony that could be present in the solution before the cathode deposit showed defects.

The antimony in the neutral electrolyte does not have any appreciable effect on the current efficiency. However, the deposit in each case has some poor qualities. The "trees" in each case are to be found as a cathode "fringe" and their length increases with time of deposition.

In addition to the "trees", the deposit sometimes went "bad". By this, I mean that the deposit does not appear metallic. This material plated out is just a "black mess". Considerable literature has been printed concerning this poor deposit. It has been termed zinc hydride (1), basic zinc sulfate (2), zinc hydroxide (3), and finely divided zinc.

1). Thompson, Practical and Theoretical Electrochemistry. (1925)

2). W. S. Sebborn, Trans. Faraday Soc. 29, 825.

The appearance of the black deposit on the cathode as an indication of the maximum concentration of antimony per liter was of no experimental value as the results were not concordant.

Table I.

Solution with 100 g. Zn as $ZnSO_4$ and 1 mg. Sb per liter.

Without Acid. C. density was the variant.

No.	C. Density amps/sq. ft.	Potential volts	C. Efficiency in per cent	Deposit
1.	5	2.68	95.4	Coarsely Crystalline
2.	10	3.00	87.5	Spongy spots
3.	15	3.15	95.5	Sponge and Sprouts
4.	20	3.30	99.0	Sponge and Sprouts
5.	25	3.70	95.5	Bright and Sprouts
6.	30	3.80	94.2	Black Sponge
7.	35	4.00	98.2	Sprouts
8.	40	4.00	98.2	Fewer Sprouts Fair Deposit

In general, as the current density was increased, the

2). Förster and Gunther, Z. Elektrochem. 5, 20.

3). N. A. Isgarishev and P. S. Titov.

deposit became better in quality.

Table II.

Solution without acid containing 100 g. Zn as $ZnSO_4$ and varying amounts of antimony per liter.

No.	Antimony mg./L.	C. Density amps/sq. ft.	C. Efficiency in per cent	Acid g./L.
1.	0.65	30	91.7	none
2.	1.00	25	96.0	none
3.	1.00	40	99.0	none
4.	103.0	35	96.6	none
5.	103.0	35	93.4	0.5
6.	103.0	35	91.4	1.0
7.	103.0	35	59.5	1.3
8.	103.0	35	81.1	27.6
9.	103.0	35	93.0	93.3
10.	103.0	35	90.2	94.56
11.	103.0	35	71.7	157.5
12.	130.0	30	97.5	none
13.	130.0	40	99.4	0.3
14.	130.0	40	93.8	0.7
15.	130.0	40	46.5	1.4
16.	260.0	30	99.2	none
17.	260.0	30	98.3	none
18.	260.0	30	97.3	none

Solution containing 100 g. Zn as $ZnSO_4$, 1.0 mg. Antimony and varying amounts of free sulfuric acid per liter.

No.	C. Density amps/sq. ft.	C. Efficiency in per cent	Free H_2SO_4 grams/liter
1.	35	91.4	3.1
2.	35	90.2	6.1
3.	35	80.4	9.3
4.	35	79.4	12.3
5.	35	73.4	15.2
6.	35	56.0	18.4
7.	35	66.0	21.4
8.	35	60.4	30.7
9.	35	46.4	42.9
10.	35	35.0	55.2
11.	35	47.4	67.5
12.	70	87.5	9.2
13.	70	71.0	27.6
14.	70	80.0	46.0
15.	70	65.5	64.4
16.	70	57.7	82.8
17.	35	79.1	9.2
18.	35	51.3	27.6
19.	35	43.0	36.8
20.	35	42.6	36.8

Table III
Continued

No.	C. Density amps/sq. ft.	C. Efficiency in per cent	Free H_2SO_4 grams/liter
21.	35	42.8	36.8
22.	35	46.2	46.0
23.	35	51.2	55.2
24.	35	42.3	64.4

The determinations 1 to 11 were made on different stock solution than those of 17 to 24. The operating conditions were different, thus accounting for the variation of results on the duplicates.

By increasing the current density, the trees are considerably increased, yet the nature of the deposit is practically the same as that with lower current density.

These results are graphically shown on Figure 2.

Arsenic in addition to the antimony was the next impurity to be added to the electrolyte. It was in the form of arsenic oxide when put in solution. The arsenic actually in solution was determined by the gravimetric method, i. e., as $Mg_2As_2O_7$.

To determine the effects of the arsenic on the zinc deposition, it was decided to first use a neutral zinc sulfate solution with one milligram of antimony per liter.

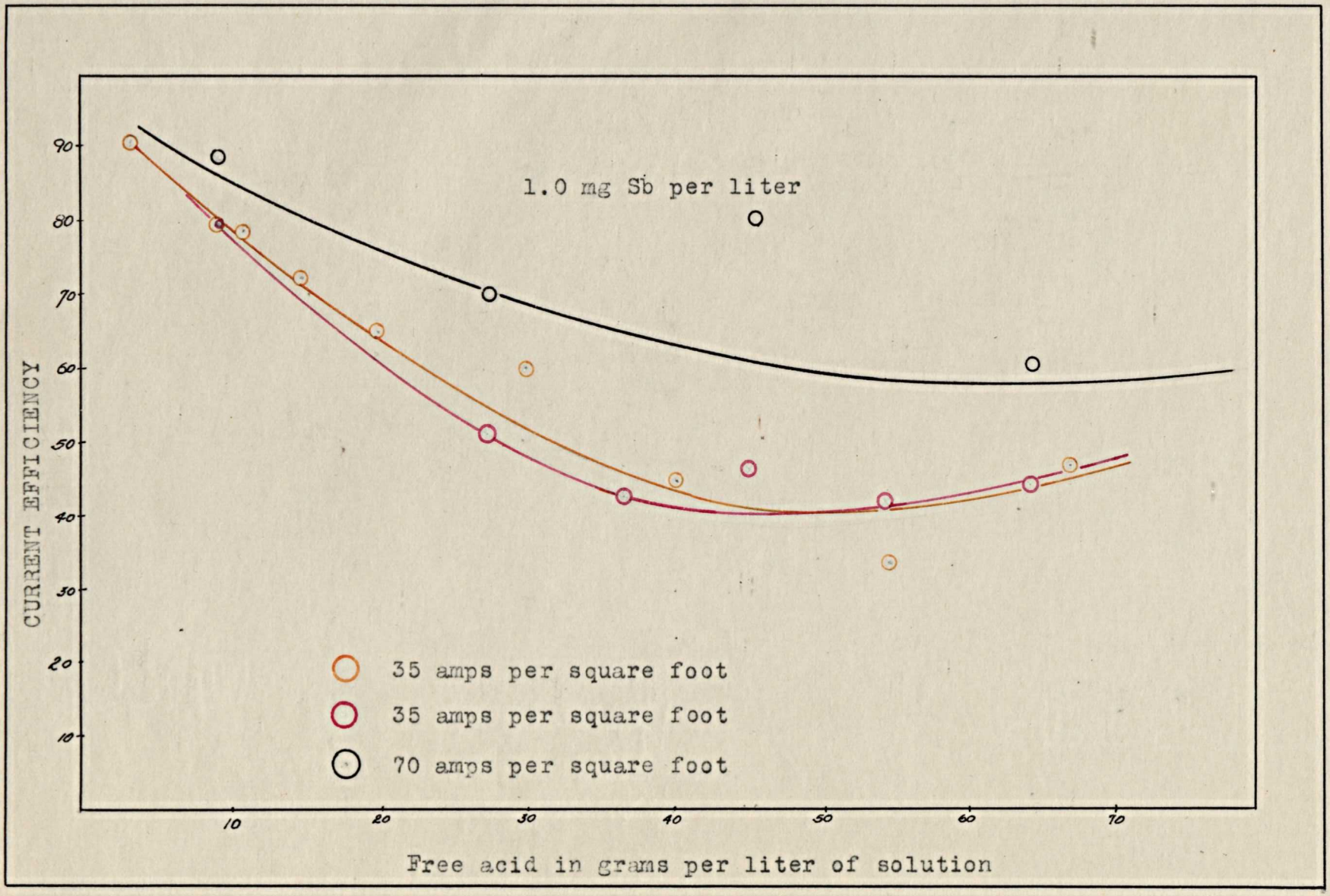

1.0 mg Sb per liter
CURRENT EFFICIENCY
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
35 amps per square foot
35 amps per square foot
70 amps per square foot
Free acid in grams per liter of solution

Figure 2

Table IV.

Solution containing 100 g. Zn as $ZnSO_4$, 1 mg. of antimony, and varying amounts of arsenic per liter. No acid added. The current density was 35 amps/square foot.

No.	Arsenic content mg./L.	C. Efficiency in per cent	Deposit
1.	1.80	94.0	Black sponge
2.	3.00	96.7	Black sponge
3.	6.00	-- #	Black slime

Not determinable.

No. 3 was the maximum amount of arsenic that could be present in the electrolyte under the given conditions. The deposit was just a slime and during electrolysis, stripped itself.

In neutral solutions, arsenic in the presence of antimony actually gave no metallic deposit on the cathode surface. The material deposited was just a sponge-like black coating. There were "trees" in each case of deposition.

Table V.

Solution containing 100 g. Zn as $ZnSO_4$, 1.2 mg. arsenic, and varying amounts of sulfuric acid per liter. Current density used was 35 amperes per square foot.

No.	Current Efficiency in per cent	Grams of H_2SO_4 per liter
1.	97.9	9.2
2.	94.8	27.6
3.	96.0	46.0
4.	90.9	64.4
5.	91.8	82.8

The zinc deposit obtained from the solution containing arsenic was of crystalline nature and did not have the "trees".

It seems that the arsenic does not appreciably lower the current efficiency when it appears as a single impurity.

Antimony and arsenic were next to be tried, to determine if the resultant mixture would, when placed in the zinc solution, cause an increase, or decrease in the current efficiency of zinc deposition. The results are to be found in table 6 and graphically on Figure 3.

Table VI.

Solution containing 100 g. Zn as $ZnSO_4$, 1.2 mg. arsenic, 1.0 mg. antimony with varying amounts of sulfuric acid per liter. The current density was 50 amperes per square foot.

No.	C. Efficiency in per cent	Free Acid gms. per L.	Deposit
1.	87.8	9.2	Small sprouts
2.	67.9	27.6	Small sprouts
3.	58.0	46.0	Buds
4.	88.7 ##	50.0	"
5.	42.2	55.6	"
6.	44.5	64.7	"
7.	61.2	90.2	"
8.	60.1	115.0	"
9.	57.0	138.0	"
10.	89.4 ##	90.2	"

These values are for ¾ hour deposits.

As the acid concentration increased in the solution, the deposit becomes more adherent, and the trees of the deposit become less in number and smaller in length.

Table VII.

Solution containing 100 g. Zn as $ZnSO_4$, 1.2 mg. arsenic, 1.0 mg. antimony and varying amounts of sulfuric acid per liter. Current density was 70 amperes per square foot.

No.	C. Efficiency in per cent	Free Sulfuric acid - gms./L.	Deposit
1.	82.4	9.2	Sprouts
2.	78.4	27.6	Less sprouting
3.	64.8	36.8	Less sprouting
4.	57.0	46.0	Less than above
5.	53.7	55.2	Just a fuzz
6.	57.7	64.4	Fine Fuzz Coarsely crystalline

The deposits obtained with higher current densities seem to be better than those obtained with lower values. The "treeing" property of the antimony has been considerably diminished. As the acid concentration approached the region of minimum current efficiency, i. e., 55 g. of acid per liter, the deposit became coarsely crystalline.

Table VIII.

Solution containing 100 g. Zn as $ZnSO_4$, 1.2 mg. arsenic, 1.0 mg. antimony, and varying amounts of H_2SO_4 per liter. The current density was 40 amperes per square foot.

No.	Current Efficiency in per cent	Free sulfuric acid - g./L.
1.	95.0	1.84
2.	90.2	3.68
3.	89.0	5.52
4.	82.2	7.36
5.	81.6	9.20
6.	72.7	13.8
7.	67.0	18.4
8.	57.5	27.6
9.	50.2	36.9
10.	32.2	46.0
11.	45.4	46.0
12.	28.5	55.2
13.	27.3	78.3
14.	32.7	92.0
15.	38.4	110.5
16.	27.8	119.5
17.	30.9	129.0
18.	38.6	132.0
19.	29.3	138.0
20.	5.0	184.0

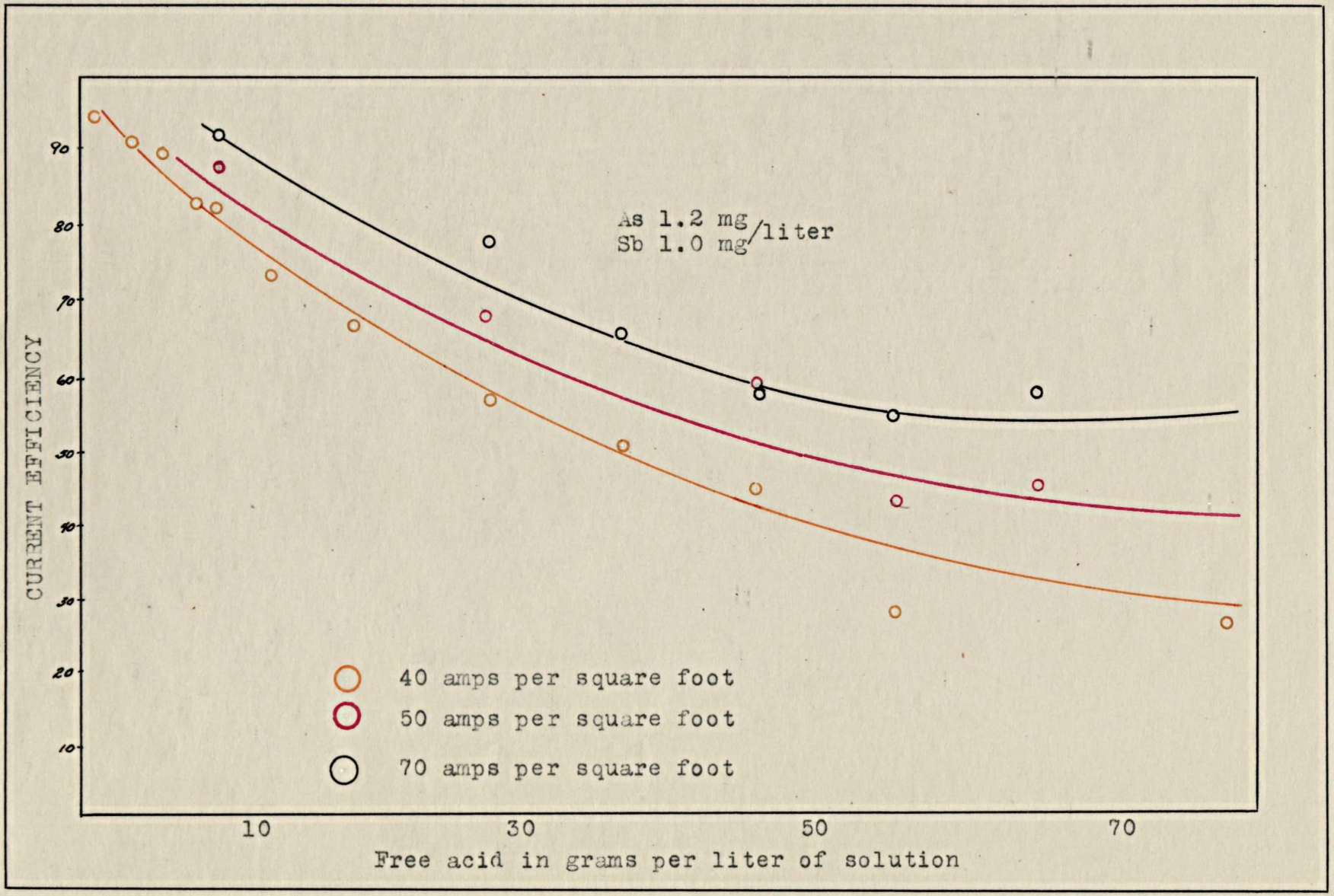

CURRENT EFFICIENCY
90
80
70
60
50
40
30
20
10
As 1.2 mg/liter
Sb 1.0 mg/liter
40 amps per square foot
50 amps per square foot
70 amps per square foot
10
30
50
70
Free acid in grams per liter of solution

Figure 3.

To draw a contrast with the above values in the last table, two depositions, using pure zinc sulfate solution with 36.8 grams of sulfuric acid per liter, were made. The current efficiencies obtained were 98.5 and 99.0 per cent. These two deposits were bright and did not have a fringe of "trees".

Cadmium and antimony in the electrolyte were next to be studied. The solutions used contained 100 g. of Zn as $ZnSO_4$, 1.0 mg. of Sb, 36.8 grams of H_2SO_4, and varying amounts of cadmium per liter. The current density used was 70 amperes per square foot. With 55 mg. of Cd present per liter, the current efficiency was 78.8 per cent. When 112 mg. of Cd was in the electrolyte, a current efficiency of 75.0 per cent was obtained. The cathode deposit was bright in each case, but the "trees" were as needles; however, they were not as numerous as when antimony alone, as an impurity, was present in the electrolyte. The current efficiency of the deposit has been increased a considerable amount by the addition of cadmium, yet its tendency to produce needles on the cathode, when it is present as an impurity, seems to offset this helpful property. A qualitative analysis to determine if Cd was in the deposited zinc was not made.

Antimonyl and potassium tartrate was added as a remedy for some of the ill effects of the antimony when it is a single impurity in the electrolyte. From the results, the "addition agent" proved to be of no merit as it added to the already poor nature of the deposit. It increased the number of "trees" and their length. The solutions used contained 100 grams of Zn as $ZnSO_4$, 1.0 mg. Sb, 36.8 g. of H_2SO_4 and varying amounts of antimonyl and potassium tartrate per liter. The current density was 70 amps per square foot. When antimony was the single impurity with solution of the above composition, and the current density was as above, a current efficiency of 65.0 per cent was obtained. When the solution of the above composition had the same conditions of operation, and 1 mg. of the "addition agent" per liter was added, a current efficiency of 65.5 per cent was the result.

Manganese sulfate was the last metallic sulfate to be added to the zinc solution. During the electrolysis of the solution, the permanganate ion is liberated and due to its strong oxidizing property, immediately oxidizes everything to the higher valence state. As soon as oxidation has taken place, the pink color becomes prominent and later decomposes and precipitates as MnO_2. The amount of $MnSO_4$ present in the solution was varied and the results are to be found on the accompanying table. Graphically, the results are on Figure 4.

Table IX.

Solution containing 100 g. Zn as $ZnSO_4$, 1.0 mg. antimony, 46.0 g. H_2SO_4, and varying amounts of manganese per liter. The current density was maintained at 40 amps per sq. ft.

No.	Current Efficiency in per cent	Mn Content mg. /liter.
1.	44.4	none
2.	75.8	45.5
3.	85.5	91.0
4.	88.9	136.5

It was found on qualitative chemical analysis, that the MnO_2 precipitated had adsorbed considerable antimony from the solution. The MnO_2 also carried a good deal of lead as the peroxide.

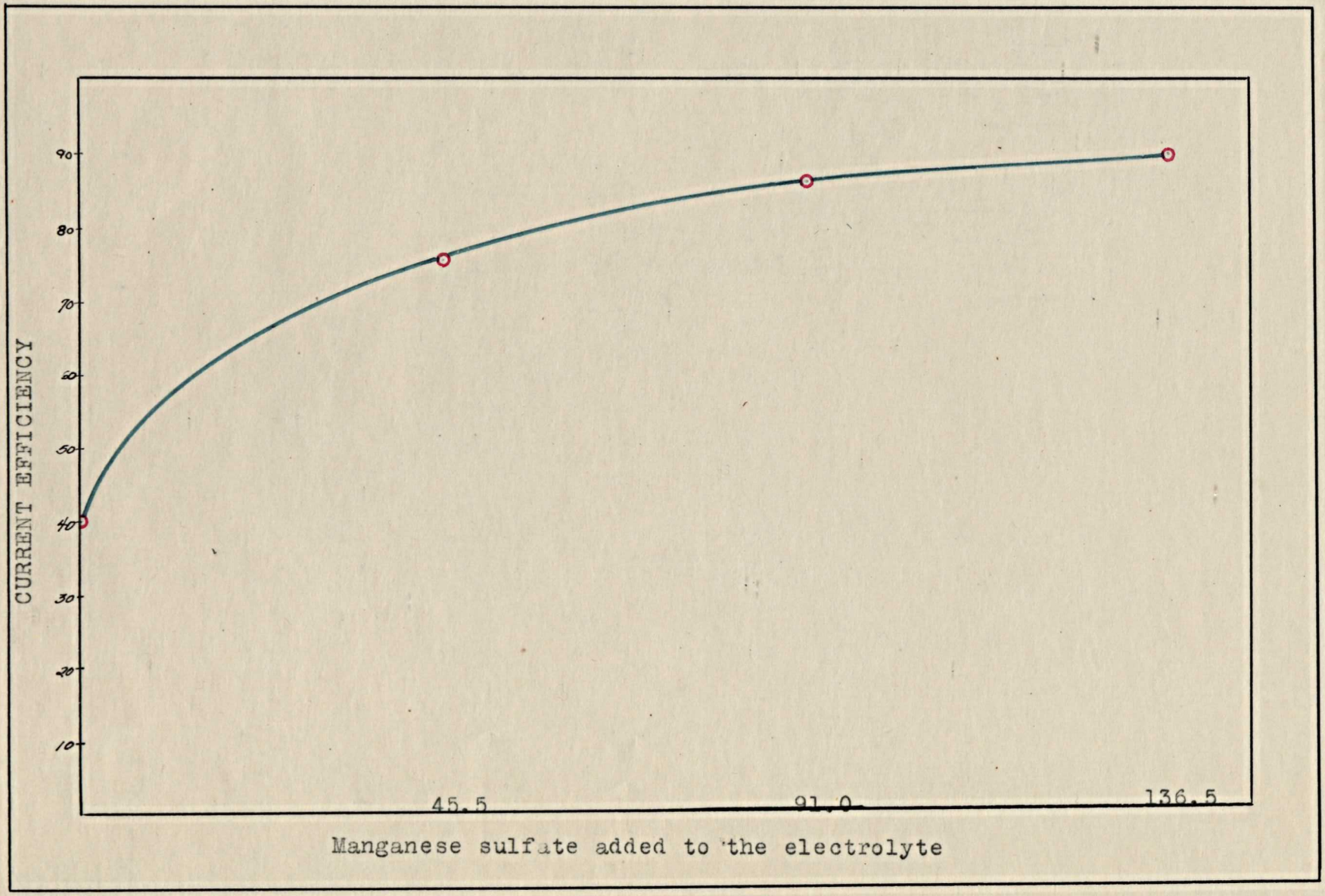

CURRENT EFFICIENCY
90
80
70
60
50
40
30
20
10
45.5
91.0
136.5
Manganese sulfate added to the electrolyte

Figure 4

CONCLUSIONS

1. Antimony actually deposits on the cathode. This can be proven by the fact that successive zinc deposition from the same solution results in better deposits and higher current efficiencies.

2. The addition of free acid to the electrolyte reduces considerably the current efficiency, but it restrains the growth of "trees" and eliminates the black spongy deposits that are poorly adherent to the cathode.

3. The addition of As, Cd, and Mn, as impurities, to an acid solution of zinc sulfate containing antimony partially restrains the growth of "trees", and results in higher current efficiencies.

4. In a neutral zinc sulfate solution, the addition of As, Cd, and Mn, as impurities, to the solution already containing antimony, invariably results in a black spongy cathode deposit. Arsenic as an impurity, in addition to the antimony in the electrolyte, was the worst offender in this respect.

5. When manganese salts are added to the zinc solution, they considerably increase the current efficiency of zinc deposition. Since MnO_2 actually has been found to adsorb the antimony, it is logical to believe that "relief" to the

cathode deposit from the impurities is not possible until nearly all the antimony has been removed from the solution, and such is the case. Prior to the prominent pink color in the solution, "trees" seem to grow with no end, however, as soon as the precipitate (MnO_2) forms, the "treeing" ends.

ACKNOWLEDGEMENT

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